

## INDEPENDENT REVIEW TEAM

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Attn: Mr. Erick R. Neher

**Subject: Numerical Value of the Soil-Water Partitioning Coefficient ( $K_d$ ) for Plutonium at the INEEL**

Dear Mr. Neher:

This letter presents the results of an independent review and evaluation conducted on-site on August 7, 2003 of the numerical value of the soil-water partitioning coefficient ( $K_d$ ) for plutonium (Pu) used for soils (not basalts) in risk assessments at various locations of the Idaho National Engineering and Environmental Laboratory (INEEL).

### OBJECTIVE OF THIS REVIEW

The objective of this review was to examine the basis for and validity of the widely differing values used for the  $K_d$  for Pu for subsurface soils at the Idaho Nuclear Technology and Engineering Center (INTEC), also known as Waste Area Group (WAG) 3, which has used a soils  $K_d$  of 22 mL/g, and the Radioactive Waste Management Complex (RWMC), also known as WAG 7, which has used a soils  $K_d$  of 5100 mL/g.

### REVIEW PROCEDURE

The review was conducted by Drs. Edgar Berkey, Peter Wierenga, and Robert Roback. Drs. Berkey and Wierenga are former members of the Groundwater/Vadose Zone Expert Panel at the Hanford site, and Dr. Roback has conducted a number of subsurface projects at the INEEL as a member of the technical staff of Los Alamos National Laboratory.

The review consisted of becoming familiar with a series of relevant documents (cited at the end of this letter) prior to (or at) an on-site meeting on August 7, 2003. During the meeting, we received a summary presentation by Dr. Larry Hull of the INEEL on the origins of the  $K_d$  values for Pu for soils at the INEEL and participated in related discussions with technical staff from both WAG 3 and WAG 7. In addition, we received the results of computer modeling studies performed at WAG 7 by Mr. Swen Magnuson of the INEEL.

that varied the value of the soils  $K_d$  for Pu and compared the results with field monitoring data.

We appreciated the high degree of cooperation displayed by all the individuals with whom we interacted. The information contained in the various documents provided to us was very useful to our review, and the presentations by Dr. Hull and Mr. Magnuson were of excellent quality.

## THE ISSUE

Pu is currently present as subsurface waste and contamination at several facilities of the INEEL. The largest known amount of Pu is present at the RWMC (WAG 7), while a much smaller quantity of Pu is present at the INTEC (WAG 3).

The numerical value used for the soil-water partitioning coefficient  $K_d$  for Pu used for subsurface soils in computer models is critical to estimating the time it will take for Pu to reach the groundwater at WAG 7, or the perched water at WAG 3, and in estimating the quantity of Pu that will reach these locations. The computer models rely on knowledge of the local subsurface geology and hydrology at the sites, as well as an estimate of how strongly Pu interacts with the various geological materials in the subsurface. The strength of this interaction can be described or symbolized by the numerical value of a partitioning coefficient or  $K_d$ .

The  $K_d$  approach is the simplest of several methods available that can be used to describe the interaction between Pu and subsurface material. This approach is often preferred because most of the other approaches require more parameter values to describe the complex subsurface interactions, and these parameter values are seldom known or available.

A high value for  $K_d$  would mean there is strong interaction (i.e., adsorption) between Pu and the surrounding geological materials, and thus, there will be very slow downward movement of Pu through the vadose zone to the groundwater or perched water. On the other hand, a low  $K_d$  value would mean less adsorption and faster downward movement.

At WAG 7, a soils  $K_d$  value for Pu of 5100 mL/g has been used for computer modeling purposes. This value for the soils  $K_d$  was based on laboratory testing with site-specific basaltic and interbed materials. The predicted result from the WAG 7 calculations is that Pu will remain tightly bound to the subsurface soils and does not pose a significant risk of migration.

However, at WAG 3, a soils  $K_d$  value for Pu of 22 mL/g has been used for computer modeling, and the results have been drastically different. This value for the soils  $K_d$  was based on adopting a conservative approach using the lowest value of this parameter from the literature, regardless of whether it was derived from representative INEEL soils. Even though WAG 3 has a significantly smaller inventory of Pu than WAG 7, the modeling results for WAG 3 show that Pu poses an unacceptable risk of migration in that location.

The major issue addressed in this review was evaluating the basis for and validity of these two values of soils  $K_d$  for Pu at the INEEL.

## OBSERVATIONS AND DISCUSSION

### **1. The soils $K_d$ for Pu used by WAG 7 (5100 mL/g) can be technically defended on several bases.**

WAG 7 has used several different approaches in establishing a soils  $K_d$  value for Pu to use at that location. These include results of batch and column studies using site-specific materials, as well as an inverse prediction method using computer modeling and comparisons with groundwater monitoring data from the field.

Batch and column studies have been performed with interbed materials and crushed basalt from the RWMC site (Newman, 1996; Dicke, 1997; Fjeld et al, 2000). Although the results showed considerable variation,  $K_d$  values were generally found to vary with the valence state of the Pu and to be higher for surface soils and subsurface interbed materials than for basalt – over 5000 for Pu(V) and above 100 for Pu(VI). For crushed basalt,  $K_d$  values were considerably lower – around 70 or a bit higher for Pu(V) and 12-24 for Pu(VI).

In their column studies, Fjeld et al (2000) found that the soils  $K_d$  for Pu(IV) and Pu(V) had values greater than 250, while lower soils  $K_d$  values were found for Pu(VI). Even though soils  $K_d$  values for Pu(VI) are generally lower, it is believed that this valence state is not stable in the INEEL environment (Cleveland, 1970; Cleveland and Rees, 1981). The value of the soils  $K_d$  for Pu of 5100 mL/g that was selected by WAG 7 is derived from the Clemson University batch tests using site-specific materials. While a range of soils  $K_d$  values for Pu(V) was observed, 5100 mL/g represented a lower bound.

Results from column studies at Clemson University (Fjeld et al, 2000; Grossman et al, 2001) also showed that a small fraction (<1%) of the Pu could be transported at a faster rate than the remainder of it. This phenomenon was more evident for basalt packed columns than for columns packed with interbed materials.

Flury et al (2003) reviewed much of the data on Pu transport. They concluded that the faster rate of transport seen in some of the column studies that have been performed may have been caused by colloids and that "significant" movement of Pu in the subsurface seems only possible if other materials or compounds are present that can facilitate Pu migration.

An inverse calculation method for assessing the value of soils  $K_d$  for Pu was also used by Mr. Magnuson at WAG 7 comparing the results with existing groundwater monitoring data for Pu from the field. A 3-dimensional flow and transport model and varying values of soils  $K_d$  were used to predict the presence of Pu in the unsaturated zone below the site and the results were compared with field data from the RWMC. The various layers consisting of basalt and interbed material at this site were reproduced in the model, and different  $K_d$  values were used for each layer. Various scenarios were run, including low, intermediate, and high soils  $K_d$  values for Pu, as well as scenarios with different fractions of fast moving Pu. It was found that in order for the model to predict the presence of Pu at 110 ft below the RWMC (where it is observed by field data), a soils  $K_d$  of 5100 mL/g had to be used in conjunction with a faster moving mobile Pu fraction ( $K_d=0$ ) for less than 1% of the inventory.

All of this provides a strong and defensible technical basis for using a soils  $K_d$  value for Pu of 5100 mL/g at WAG 7.

**2. The soils  $K_d$  for Pu at WAG 3 used to date (22 mL/g) cannot be technically defended as the basis for future detailed risk calculations, and its use will result in predicted risks that are over-stated and not supported by field measurements.**

To date, a soils  $K_d$  value for Pu of 22 mL/g has been used in modeling studies for WAG 3. This value was selected for the original assessment of WAG 3 as being a conservative approach in accordance with the INEEL's Track 2 Site Screening Guidance for low probability hazard sites. Apparently, 22 mL/g was the smallest value of  $K_d$  for Pu found in the literature when it was selected, although its value was determined using crushed basalt (not even subsurface soil) from Hanford and synthetic groundwater at pH 10, both conditions of which are not representative of the INEEL site (reported in Olsen et al, 1999).

Also presented in Olsen et al (1999) is information that clearly identified the technical indefensibility of using a soils  $K_d$  value for Pu of 22 mL/g in more definitive modeling studies for WAG 3. However, the information was apparently not heeded at the time, or subsequently.

While use of a conservative approach in screening calculations is certainly an acceptable methodology, when preliminary risk assessment results using such an approach indicated the presence of risk from Pu migration, as they did at WAG 3, much closer examination of the technical assumptions was warranted. The value selected for more definitive risk calculations for such an important parameter as the soils  $K_d$  for Pu should be highly defensible on technical grounds and represent the best available number, not the value derived for use in a generic conservative process.

The value of 22 originally selected for the soils  $K_d$  of Pu was not intended to be definitive for WAG 3, nor it should become so. Continued use of this low value for soils  $K_d$  at WAG 3 for future risk calculations is not technically defensible. The number was determined from studies using crushed basalt that is not representative of the layers of alluvial soils, basalt and interbed materials present at WAG 3. Further, it was not based on site-specific findings from either laboratory or field studies or derived from site-specific inverse modeling studies that compared the results with available groundwater monitoring data from the INTEC site.

Use of a soils  $K_d$  for Pu of 22 mL/g for risk calculations at WAG 3 should cease immediately, and efforts must be put into place to determine a more representative and accurate value for this parameter.

3. The near-term objective should not be to establish the "correct" value of soils  $K_d$  for Pu to use at WAG 3 but only to establish a minimum technically defensible value, while further studies are performed.

Although there are some differences between WAG 3 and WAG 7 in subsurface stratigraphy and composition of geological materials, there are also many similarities. It is very unlikely that the differences would result in a soils  $K_d$  for Pu at WAG 3 that is 232 times lower than at WAG 7, since this represents an enormous difference in the ability of the subsurface soil to retard the movement of Pu.

Based on the available batch and column data, it is probably safe to say that soils  $K_d$  values for Pu in the subsurface of both WAG 3 and WAG 7 are greater than 250 mL/g. It would be highly informative to determine what the modeling results at WAG 3 would show using a soils  $K_d$  for Pu of 250 mL/g. Additionally, it would be informative to determine the results from inverse modeling compared with existing groundwater monitoring data from WAG 3.

Site-specific data relative to the soils  $K_d$  for Pu for the INTEC site (WAG 3) are much more limited than for the RWMC (WAG 7). Thus, additional studies specifically for the INTEC site seem warranted.

Over the past years, INEEL has made a good effort in funding relevant laboratory and field studies at WAG 7, as well as in summarizing the Pu studies and data applicable to the RWMC. A related effort at WAG 3 may be in order because of the current implications arising from the site screening risk assessment and the large magnitude of potentially unnecessary expenditures that might be triggered as a result.

## CONCLUSIONS

1. A soils  $K_d$  value for Pu of 5100 mL/g for WAG 7 is technically supportable and defensible based on several different lines of relevant evidence.
2. There is no defensible technical basis to continue using a value of 22 mL/g for the soils  $K_d$  for Pu of at WAG 3, as there is considerable evidence from both the literature and the field that it is much higher. Use of this value will result in risks from Pu that are over-stated and not consistent with field measurements.
3. Continued use of a numerical value for the soils  $K_d$  for Pu for definitive flow and transport predictions that was originally selected in accordance with a conservative screening methodology is not scientifically justifiable or technically defensible, and it should cease.
4. Based on information available in the literature, and the batch, column, and modeling data from WAG 7, a soils  $K_d$  value for Pu of at least 250 mL/g would be a much better first estimate for WAG 3 in future risk assessment calculations while additional work is performed to determine a more representative value.
5. It would be very advantageous for the INEEL to develop a consistent position with respect to the  $K_d$  value for Pu on-site. The differences (if any) between the soils  $K_d$  value for Pu used at WAG 7 must be rationalized with the soils  $K_d$  value for Pu used at WAG 3. This likely cannot be done without some site-specific work involving WAG 3.

## RECOMMENDATIONS

1. As part of developing a consistent position for INEEL on the  $K_d$  value for Pu, the information presented by Dr. Larry Hull should be compiled and published in an official report that should be peer reviewed by persons competent in Pu chemistry and subsurface transport.

2. WAG 3 staff should cease use of 22 mL/g as the value of the soils  $K_d$  for Pu in risk assessments. While a more representative number is being developed by site-specific studies, a series of risk assessment studies using technically traceable values of soils  $K_d$  for Pu of 110 mL/g, and 250 mL/g should be performed to provide information on the sensitivity of the results to this parameter.
3. WAG 3 staff should initiate inverse modeling studies of Pu transport below the INTEC site using a range of soils  $K_d$  values for Pu and fast-moving fractions of Pu and compare the results with existing groundwater monitoring data, similar to the work performed by Mr. Magnuson for the RWMC (WAG 7) site. Site-specific geological and hydrological information should be used in this effort, and initially, a one-dimensional flow and transport model should be used. The purpose of this modeling would be to determine a lower bound for a representative soils  $K_d$  value for Pu at this site.
4. If the results of the sensitivity analysis and inverse modeling efforts indicate the potential that Pu could still exceed Remedial Action Objectives in groundwater beneath INTEC, then the modeling effort should be supported with additional batch and column studies using basalt and interbed materials from the INTEC site. In addition, there is a need for further information regarding the predominant chemical form(s) and oxidation state(s) of Pu in soil at INTEC. If required, these studies can be done either in parallel with the modeling studies, or following the modeling studies.
5. We also support publication and peer review of a document in which a comparison is made of the geological and hydrological information available for the subsurface below the RWMC and INTEC sites. Although we expect that the stratigraphy may differ somewhat, the alluvium, basalt and interbed sediments at both sites are likely more similar than different. Once the information from both sites is available, it will make comparisons between the two sites more clear and provide better technical justification for drawing conclusions for either site using data from the other. If after a thorough search, comparable information from the two sites does not exist, then a study could be initiated to compare and contrast WAG 7 subsurface material with WAG 3 subsurface material.

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This concludes our review of this matter. Please advise if you have any questions or need any clarifications regarding our views.

Mr. Erick R. Neher  
August 28, 2003  
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Yours very truly,

*Original signed by Dr. Berkey on behalf of the Independent Review Team*

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